EXHIBIT 6

A re-evaluation of the taste and odour of methyl tertiary butyl ether (MTBE) in drinking water

I.H. Suffet

Environmental Science and Engineering Program, School of Public Health, University of California, Los Angeles, Los Angeles, CA 90095-1772, USA (E-mail: *msuffet@ucla.edu*)

Abstract Methyl tertiary butyl ether (MTBE) is a gasoline additive that has been found in groundwater when an underground gasoline storage tank leaks. Although dependent on the clean-up standards that are applied, clean-up costs have been estimated in the US alone to be in the billions of dollars. MTBE is considered primarily a taste and odour concern and not a toxicity issue at concentrations found in drinking water. Thus, the clean-up of MTBE problems is controlled by the MTBE odour threshold concentration (OTC). The level of clean-up and associated differential of millions of dollars is a matter of concern for water purveyors and well owners. A 1993 study of nine OTC studies showed the OTC of MTBE in water to be between 0.04 and 0.06 μg/L, a level over two orders of magnitude less than eight other studies. This 1993 study was repeated at the original laboratory in 2004 and is reported in this paper. The laboratory's quality control programme and ability to repeat one of the eight other studies indicated the laboratory was qualified to repeat its original OTC study. The flavour and odour detection threshold range in the 1993 study, however, could not be confirmed by trained assessors repeating the original study in 2004. The inconsistencies in the data and the high detection on water blanks indicate that the dilution series of the test solutions for the 1993 study were mainly at subthreshold levels. Therefore, the original study of 1993 is not a valid OTC study for MTBE and should not be used to develop drinking water and clean-up standards. The OTC of MTBE is over 15 μg/L for the eight valid studies.

Keywords MTBE; odour threshold concentration (OTC); OTC determination

Water Science & Technology Vol 55 No 5 pp 265–273 © IWA Publishing 2007

Introduction

Methyl tertiary butyl ether (MTBE) is a gasoline additive used to reduce smog formation. In 1998, MTBE accounted for 85% of all oxygenates used in the US or roughly 15 billion litres per year (EPA, 1999). MTBE is very soluble in water, and as a result, when an underground storage tank of gasoline leaks, MTBE has been found in groundwater along with other gasoline components (e.g. Squillace *et al.*, 1996; Shih *et al.*, 2004). For example, Shih *et al.* (2004) has presented an example of the widespread problems and plume length at leaky underground tank sites located in the greater Los Angeles region.

MTBE is considered primarily a taste and odour concern and not a toxicity issue at the levels found in drinking water. Thus, setting drinking water standards for MTBE has become an issue for drinking water regulators, as most recently reviewed in Canada (Canadian Government, 2005). In Canada, a drinking water guideline based upon odour threshold assessments was proposed at 15 μg/L. Although dependent on clean-up standards, clean-up costs have been estimated in the US alone to be in the billions of dollars. Thus, the basis for clean-up of MTBE problems is the odour threshold concentration (OTC). The level of clean-up and associated differential of millions of dollars is a matter of concern for water purveyors and well owners. Therefore, the OTC must be based on good science and be scientifically defensible. Currently, there is no consensus regarding an OTC-based drinking water standard in the US.

doi: 10.2166/wst.2007.188

Objectives

Table 1, based upon McGuire (2003) and Stocking *et al.* (2001), shows nine studies that have been completed on the OTC of MTBE. Eight have OTC near or above 15 μg/L. The OTC study conducted by Campden Food and Drink Research Association (Campden, 1993) stands out as extremely different from the other studies. The result of this work states: "The concentration at which 70% of an experienced panel can detect the flavour of MTBE in water is between 0.04 and 0.06 ppb". The MTBE levels studied (0.001–10 μg/L) and the odour threshold were much lower than all other studies. Is the Campden (1993) study correct and should it be used as part of the database to set an MTBE taste and odour limit for drinking water? The objective of this evaluation was to use the same laboratory that performed the original Campden (1993) study, repeating that study using quality assurance (QA) methods to determine whether the original study was scientifically valid. This Campden (1993) study was repeated at the original laboratory and is reported in this paper as the Campden (2004) study. The Stocking *et al.* (2001) study was repeated by Campden as one quality assurance test of the laboratory (Campden, 2003).

Methods

The Stocking *et al.* (2001) and the Campden (2003) study used the ASTM Method Standard E-679-91 (ASTM, 1991) to determine the OTC by a consumer (untrained) panel. The E-679-91 Method (ASTM, 1991) states that: "The panel threshold is the geometric mean of the best-estimated thresholds of the individual panelists". Expert panels utilise people who have been trained, have increased sensitivity, and should represent the more sensitive proportion of the general population. The odour or flavour threshold concentrations determined by an expert panel should be more reproducible than untrained consumers. There are seven steps for the preparation of the concentration scale under the E-679-91 Method (ASTM, 1991). The key parts of the seven steps are:

1. The concentration levels of MTBE in water "should begin well below the level at which the most sensitive panelist is able to detect or recognize the added substance and end at (or above) the concentration at which all panelists give a correct response".
2. "Good judgment is required ... to determine the appropriate scale steps range .... This might involve the preparation of an approximate threshold concentration ... "
3. "In actual practice, the various concentrations are obtained by starting at the highest concentration and diluting three times per step, thus providing a series of dilution factors ... "

The study by Stocking *et al.* (2001) for the determination of the OTC by an untrained consumer panel is an example of the use of the ASTM Method E-679-91. Figure 1 represents a typical data output from the study. Over 80% of the panelists gave a correct answer for the highest concentration. Thus, one rule was not followed for this study. However, the four previous literature studies, used to select the initial concentration, showed that expert panels should detect a 100 μg/L concentration.

Results and discussion

The Campden (2003) quality assurance study was completed to see if the Camden Laboratories could reproduce the Stocking *et al.* (2001) study. The Campden (2003) study used an ascending concentration method with a consumer panel to determine the odour or flavour (flavour-by-mouth or sipping and swirling the sample in the mouth) threshold concentration.

Blank waters were tested at random in the ascending series. The determination included false positives, i.e. the per cent of the time that the panel detected a positive for blank water. The ascending series concentration method measures the per cent of the

Table 1 Summary for threshold determinations of MTBE in water

No.	Authors	Year	Subjects	Panel	Type test	Type of water	T/O	Water temp.	No. sample tested	Concentration range (μg/L)		Threshold results (μg/L)	Odour quality
1a	TRC/ARCO	1993	7	T	FCT	DW	O	Unk	5 (2 rounds)	106	1,483		
1b	TRC/ARCO	1993	6	T	PC	DW	T	Unk	6 (2 rounds)	106	1,483		
2a	TRC/API	1993	7	T	FCT?	DW	O	Unk	6 (2 rounds)	23	740		
2b	TRC/API	1993	7	T	PC	DW	T	Unk	6 (2 rounds)	23	740		
3	Prah	1994	38	UnT	FCT?	DW	O	Unk	6 binary dilutions	Unk (stable at 0.1%)	Unk	180 (50% of panel)	NA
4a	Young	1996	9 F	T	PC	Still, natural, mineral	T	25°C	6	Unk	Unk	48[2]	Estery, bitter
4b	Young	1996	9 F	T	PC	Still, natural, mineral	O	40°C	6	Unk	Unk	34[2]	Estery, vanilla, sweet
5a	Shen	1997	8–10	T	SM?	OFW w/free $Cl_2 = 0.2$ mg/L	O	40°C	Unk	2.5	50	20.9[2]	NA
5b	Shen	1997	8–10	T	SM?	Tap w/free $Cl_2 = 0.2$ mg/L	O	40°C	Unk	15	50	17.4[2]	NA
5c	Shen	1997	8–10	T	SM?	OFW	O	40°C	Unk	5	100	28.5[2]	NA
5d	Shen	1997	8–10	T	SM?	OFW	O	40°C	Unk	15	150	35.3[2]	NA
5e	Shen	1997	8–10	T	SM?	OFW w/free $Cl_2 = 0.2$ mg/L	O	Room	Unk	5	100	31.3[2]	NA
5f	Shen	1997	8–10	T	SM?	OFW w/free $Cl_2 = 0.2$ mg/L	O	Room	Unk	15	100	43.5[2]	NA
5g	Shen	1997	8–10	T	SM?	Tap w/free $Cl_2 = 0.2$ mg/L	O	Room	Unk	2,5	100	13.5[2]	NA
5h	Shen	1997	8–10	T	SM?	Tap w/free $Cl_2 = 0.2$ mg/L	O	Room	Unk	2,5	150	33.9[2]	NA
5i	Shen	1997	8–10	T	SM?	OFW	O	Room	Unk	5	100	22.6[2]	NA
5j	Shen	1997	8–10	T	SM?	OFW	O	Room	Unk	15	100	40.3[2]	NA
5k	Shen	1997	8–10	T	SM?	OFW	O	Room	Unk	2.5	100	15.6[2]	NA
5l	Shen	1997	8–10	T	SM?	OFW	O	Room	Unk	2.5	100	13.5[2]	NA

cont.

Table 1 (*continued*)

No.	Authors	Year	Subjects	Panel	Type test	Type of water	T/O	Water temp.	No. sample tested	Concentration range (μg/L)		Threshold results (μg/L)	Odour quality
6a	Dale	1997	4	T	FPA	OFW	O	25°C	7	2	190	90–100	Sweet, solvent
6b	Dale	1997	4	T	FPA	OFW	T	25°C	7	2	190	50	Sweet, solvent
6c	Dale	1997	4?	T	FCT	OFW	O	25°C	7	6	118	43–71[1]	NA
6d	Dale	1997'	4?	T	FCT	CRW	T	25°C	5	3	61	26–58[1]	NA
6e	Dale	1997	4?	T	FCT	OFW	T	25°C	9	2	76	24–37[1]	NA
7	Stocking *et al.*	2001	57	C	FCT	OFW	O	Room	8	2	100	15[2]	NA
8a	McGuire	2000	1	T	FPA	Bottle water	O	25°C	7	2	60		
8b	McGuire	2000	1	T	FPA	Bottle water	O	25°C	7	2	60		
9	Campden	1993	12	T	ACM	Bottle water	O	Room 18°C	4–5 (3 trials)	0.001	10	70% Detect 0.36–0.48	
9	Campden	1993	12	T	ACM	Bottle water	T	Unk	4–5 (3 trials)	0.001	10	70% Detect 0.04–0.06	

[1]Mean ± 1 Standard deviation, 60% probability; ACM, ascending concentration method; C, consumer; CRW, Colorado River water; DW, distilled water; F, females; [2]geometric mean; FCT, force choice trial; OFW, odour free water; SM, standard methods of water and wastewater; NA, not available; O, odour; PC, paired comparison; T, trained; T/O, taste and odour; Unk, unknown; UnT, untrained

NYC-SUFFET-000659

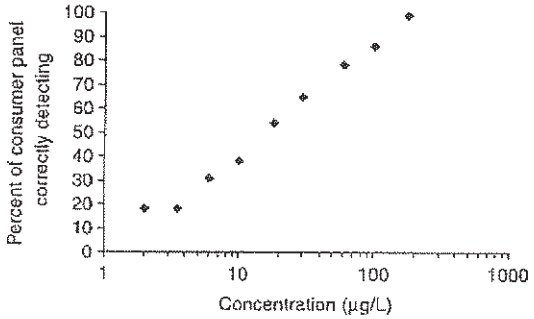

Figure 1 Presentation of data for the odour detection of MTBE – using consumers (Stocking *et al.*, 2001)

expert panel that correctly detects an odour versus the increasing concentration of the odorant added to determine the OTC in water.

Figure 1 shows that the values in the Stocking *et al.* (2001) study ranged from 2 to 100 µg/L with a geometric mean of 15 µg/L. Figure 2 shows that for consumers in the Campden (2003) study, the odour threshold detection level of 52.7 µg/L represents the average threshold of approximately 56% of the consumers which apparently accounts for false positives (Campden, 2003). The data show that only 60% of the consumer population gave a correct answer for the highest concentration. The panel in the Campden (2003) study was not as sensitive as the panel in the Stocking *et al.* (2001) study. However, the Campden (2003) consumer panel determination of the odour detection of MTBE was within experimental error range of the Stocking *et al.* (2001) consumer panel study result of 15 µg/L. In fact, the 50% of the total consumer population value was 18 µg/L, which can be interpreted as the OTC for the Campden (2003) study. The actual concentrations presented to the panelists were determined by chemical analysis for both the Stocking *et al.* (2001) and Campden (2003) studies. The data from the Campden (2003) study matche the range of concentrations found by other studies, except the Campden (1993) study (see Table 1). Campden (2003) had good quality assurance for the Campden Laboratories and is a valid data set that can be added to Table 1.

Figure 3a and b (odour) and Figure 4a and b (flavour) compare the original Campden Food and Drink Research Association (Campden, 1993) and the repeat of these studies by the same organisation, now known as the Campden and Chorleywood Food Research Association (Campden, 2004). It should be noted that in Figures 3a, 3b, 4a and 4b the

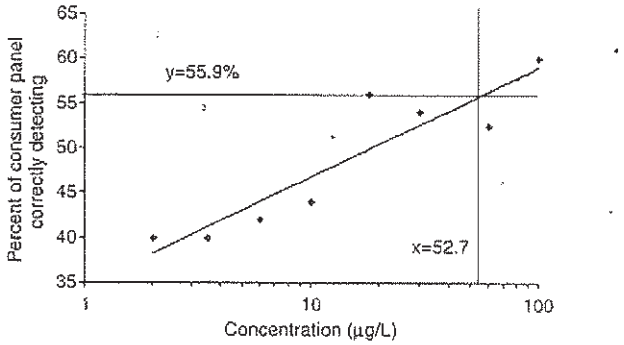

Figure 2 Presentation of data for the odour detection of MTBE – using consumers (Campden, 2003)

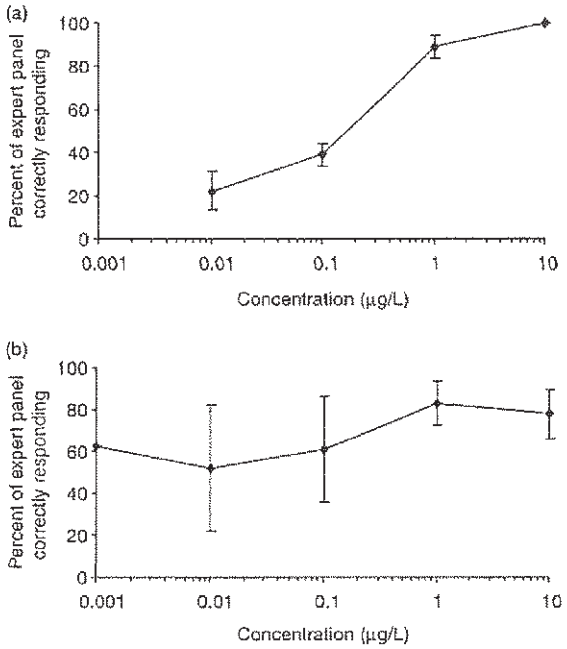

Figure 3 (a) Odour detection of MTBE by Campden (1993). The study was repeated three times with 13 panelists. Average ± standard deviation (SD) of three panel runs. (b) Odour detection of MTBE by Campden (2004). The study was repeated six times with 12 panelists. Average ± SD of six panel runs

error bars are not present in some cases because insufficient data points were available to calculate standard deviations (SD). Also, it should be noted that all odour panel studies did not use the exact same concentrations.

The Campden (1993) study shows the expected panel response in Figure 3a and b, i.e. a straight-line relationship between the percentage of panelists correctly responding to a known concentration plotted on a log scale. Campden (1993) reported: "The concentration at which 70% of an experienced panel can detect the flavour of MTBE in water is between 0.04 and 0.06 ppb". The MTBE levels studied by Campden (1993) were much lower (0.001–10 µg/L) than all other laboratories and the odour threshold was much lower than all other laboratories (see Table 1). Upon review of the study, insufficient quality assurance was indicated as no chemical analysis was completed to verify the MTBE concentrations that were presented to the panel. For example, a dilution error of 100-fold could be possible.

The Campden (1993) study was repeated by Campden (2004). The results of a first trial of tests in the Campden (2004) study of flavour and odour thresholds showed no consistent pattern and a threshold range could not be calculated with confidence (Campden, 2004). Although Campden (2004) concluded, after conducting a number of quality checks (including the chemical determination of MTBE concentrations after every dilution), that errors had not been introduced in the way in which the test was administered, it was decided to run, with new trained assessors, a second trial to assure that errors had not been introduced in the preparation of the samples used. The results from the second trial of flavour and odour threshold tests were similar to the first trial in that there was no consistent pattern and, again, a threshold range could not be calculated with confidence (Campden, 2004).

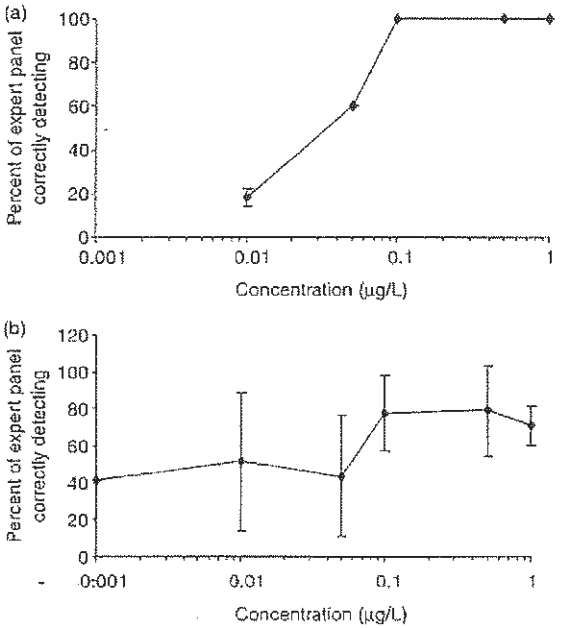

Figure 4 (a) Flavour detection of MTBE by Campden (1993). The study was repeated three times with 12–13 panelists. Average ± SD of three runs. (b) Flavour detection of MTBE by Campden (2004). The study was repeated six times with 12 panelists. Average ± SD of six runs

Chemical analysis confirmed the MTBE concentrations in the solutions were within acceptable analytical chemical error in the Campden (2004) study. Two different expert panels of 12 individuals each took part in the Campden (2004) study. False positives were found for background water indicating the panel could be mistaking background water for MTBE levels. Figures 3b and 4b summarise all the data from two runs of each panel. The conclusion reached by Campden (2004) was: "A flavour and odour detection threshold range could not be confirmed for MTBE in water for trained assessors using this dilution series. The inconsistencies in the data and the high detection on the water blanks may indicate that the dilution series of the test solutions for this study were mainly at sub-threshold levels". Unfortunately, it is not possible to confirm the dilution series in the 1993 study as no analytical confirmation of MTBE concentrations in solution was carried out in then. Therefore, the Campden (1993) study is not a valid OTC study for MTBE and should not be used for the purpose of setting drinking water or clean-up standards. Campden (2004), having adequate quality assurance, is a valid data set. However, no odour threshold for MTBE could be determined from the data.

Table 2 shows the comparison of the four studies presented in this paper. The 2004 Campden flavour and odour detection threshold range could not confirm the Campden (1993) study of MTBE in water for trained assessors. The inconsistencies in the data and the high detection on water blanks indicate that the dilution series of the test solutions for the 1993 study were mainly at subthreshold levels. Therefore, the original study of 1993 is not a valid OTC study for MTBE and should not be used to develop drinking water and clean-up standards. The OTC of MTBE is over 15 µg/L for the eight valid studies as shown in Table 1.

Table 2 Summary of MTBE studies presented in this paper

Study name	Method	Quality assurance	OTC[1] (μg/L)	Study validity	Comments
Campden (1993)	ACM[2]	Inadequate	0.04–0.06	Poor	Remove from Table 1
Stocking *et al.* (2001)	ASTM Method No. E679-91	Yes – chemical and panel	15 μg/L	Good	Leave in Table 1
Campden (2003)	ASTM Method No. E679-91	Yes – chemical and panel	18 μg/L[3]	Good	Add to Table 1
Campden (2004)	ACM[2]	Yes – chemical and panel	None determined	Poor	Could not reproduce Campden (1993) study

[1]OTC (odour threshold concentration) reported is the geometric mean value
[2]ACM (ascending concentration method)
[3]See geometric mean of Figure 2

Conclusions

The following conclusions were drawn from this comparison of MTBE OTC studies:

1. The Campden (2004) results of OTC with an expert panel could not validate the Campden (1993) study. Therefore, the Campden (1993) study is not a valid study and should not be used for the purpose of setting drinking water or clean-up standards.
2. The dilution series of the Campden (2004) study was validated by chemical analysis of MTBE after each dilution. The Campden (1993) study cannot be verified because no analytical confirmation of MTBE concentrations in solutions were carried out.
3. The Campden (2003) consumer panel determination of the odour detection of MTBE was within the error range of the Stocking *et al.* (2001) consumer panel study result of 15 μg/L. The Campden (2003) study with good quality assurance is a valid data set for Table 1.
4. Table 1 shows that eight studies of the OTC of MTBE and the Campden (2003) study agree that the OTC is at or above 15 μg/L.
5. MTBE levels for drinking water and clean-up standards should be based on an OTC at μg/L levels as shown in the consumer studies of Stocking *et al.* (2001) and Campden (2003).

References

American Petroleum Institute (1994). *Odor Threshold Studies Performed With Gasoline and Gasoline Combined with MTBE, ETBE, and TAME*. API Pub. 4592, Washington, DC., USA.

ARCO Chemical Co. (1993). *The Odor and Taste Threshold Studies Performed with Methyl Tertiary Butyl Ether and Ethyl Tertiary Butyl Ether*. Windsor, Canada.

ASTM (1991). *Standard Practice for Determination of Odor and Taste Thresholds by Force-choice Ascending Concentration Series Method of Limits* (E679-91). American Society for Testing and Materials, Philadelphia, PA, USA.

Campden (1993). *Flavour and Odour Thresholds of Methyl Tertiary Butyl Ether (MTBE) in Water*. Campden Food and Drink Research Association, UK. Report Number S/14084/01.

Campden (2003). *Consumer Odour Threshold of Methyl Tertiary Butyl Ether (MTBE) in Water*. Campden and Chorleywood Food Research Association, UK. Report Number S/REP/ 74638/2, (available from author I.H. Suffet).

Campden (2004). *Flavour and Odour Thresholds of Methyl Tertiary Butyl Ether (MTBE) in Water*. Campden and Chorleywood Food Research Association, UK. Report Number S/REP/74638, (available from author I.H. Suffet.).

Canadian Government (2005). *MTBE in Drinking Water- Public Comment Document*, Ottawa, Canada.

Dale, M.S. (1997). MTBE taste-and-odor threshold determination using the flavor profile method. In: *Proceedings American Water Works Assoc., Water Quality Technology Conf.*, Denver, CO, USA. November.

EPA (1999). *The Report of the Blue Ribbon Panel on Oxygenates in Gasoline*. US Government Printing Office, Washington, DC, USA. EPA Report 420-R-99-021.

McGuire, M.J. (2003). *Summary of Threshold Determinations for MTBE in Water*. Exhibit Bates number: DEXP-MJM 015685.

Prah, J.D. (1994). Sensory, symptomatic, inflammatory, and ocular responses to and the metabolism of methyl tertiary butyl ether in a controlled human exposure experiment. *Inhal. Toxicol.*, 6, 521–538.

Shen, Y.F. (1997). *Threshold Odor Concentrations of MTBE and Other Fuel Oxygenates*. Fountain Valley, CA, USA. Research Report of Orange County Water District.

Shih, T., Rong, Y., Harmon, T. and Suffet, I.H. (2004). Evaluation of the impact of fuel hydrocarbons and oxygenates on groundwater resources. *Env. Sci. Tech.*, 38, 42–48.

Squillace, P.J., Zogorski, J.S., Wilber, W.G. and Price, C.V. (1996). Preliminary assessment of the occurrence and possible sources of MTBE in groundwater in the US, 1993–1995. *Env. Sci. Tech.*, 30, 1721–1730.

Stocking, A., Suffet, I., McGuire, M.J. and Kavanaugh, M. (2001). Implications of a MTBE consumer threshold odor study for drinking water standard setting. *J. AWWA*, 93(3), 95–105.

Young, W.F. (1996). Taste and odor threshold concentrations of potential potable water contaminants. *Wat. Res.*, 30(2), 331.